CO₂ Capture by enzyme inspired solid sorbents – a new innovative approach.

Karl Petter Lillerud
inGAP – University of Oslo
Norway

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The catalysis group – Research 2013

Stian Svelle K.-P. Lillerud Unni Olsbye  Ole Swang  Silvia Bordiga  Mats Tilset

Heterogeneous catalysis  Quantum chemistry  Spectroscopy  Homogeneous catalysis

• Materials based catalysis research.
  • Natural gas to Chemicals (plastic and fuels)
  • CO₂ to Chemicals (New activity 2010)
  • Gold complexes in Homogeneous catalysis.
The anthropogenic Nitrogen cycle is as large as the natural cycle.
Anthropogenic Chemical Carbon Cycle

Anthropogenic Chemical Carbon Cycle for a Sustainable Future

CO₂ separation and Capture technologies

- Absorption
  - Chemical
    - MEA, DEA
    - KOH, NaOH, MgO
    - Etc.
  - Physical
    - Solexol
    - Rectisol
    - Etc.

- Adsorption
  - Alumina
  - Zeolite
  - Activated carbon

- Cryogenics
  - Dry ice formation at low temperature

- Membranes
  - Polymer based
    - Poly(phenylene oxide)
    - Poly(ethylene oxide)
    - Poly(ionic liquid)
  - Inorganic membranes
    - Ceramic based
    - Zeolite based

- Algal and microbial systems

Regeneration method
- Pressure swing
- Temperature swing
- Moisture swing
- And combination thereof

Metal Organic Framework Materials, MOFs

Catalysis or Processes

Homogen, Amine (MEA) process

- Solution
- Catalyst or MEA

Heterogen - solid sorbents

- Reactants
- Product(s)
- Solid catalyst of sorbent

Enzymes - Natures way

RuBisCo
CO$_2$ separation and Capture technologies

Energy - Cost of todays technologies

Table 1. Estimated Energy Required To Remove and Recover CO$_2$ from Coal-Fired Power Plants Using Various Technologies$^{36}$

<table>
<thead>
<tr>
<th>process</th>
<th>CO$_2$ removal efficiency (%)</th>
<th>kWh(e)/lb CO$_2$ recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Improved amine absorption/stripping</td>
<td>90</td>
<td>0.11</td>
</tr>
<tr>
<td>integrated plant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen/coal-fired power plant</td>
<td>100</td>
<td>0.15</td>
</tr>
<tr>
<td>Amine (MEA) absorption/stripping</td>
<td>90</td>
<td>0.27</td>
</tr>
<tr>
<td>nonintegrated plant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium carbonate absorption/stripping</td>
<td>90</td>
<td>0.32</td>
</tr>
<tr>
<td>Molecular sieves adsorption/stripping</td>
<td>90</td>
<td>0.40</td>
</tr>
<tr>
<td>Refrigeration</td>
<td>90</td>
<td>0.40</td>
</tr>
<tr>
<td>Seawater absorption</td>
<td>90</td>
<td>0.80</td>
</tr>
<tr>
<td>Membrane separation</td>
<td>90</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Zeolite based
New solid sorbents has to be 2-4 times better in order to compete!

Catalysts compared with sorbents

Energy vs. Reaction coordinates

Adsorption

Desorption

Reaction
Catalysts compared with sorbents

Energy vs. Reaction coordinates

Adsorption

Desorption
Catalysts compared with sorbents

Parameters to be optimized:

1. Adsorption capacity, Number of sites / gram or cm$^3$

2. Sorption enthalpy

$\Delta H$ (kJ/mol)
High Adsorption capacity = large surface

**NanoPorousMaterials - Zeotypes**

Surface is an oxide $\text{SiO}_2$, $\text{AlSiO}_4$, $\text{AlPO}_4$

CHA topology, 3D-8 ring structure

Pore size of molecular dimension (3-12 Å)

201 different topologies are known (2012)
High Adsorption capacity = large surface

**NanoPorousMaterials II - MOFs**

MOF based; surface are mostly organic, and with "lego" possibilities to include functional groups.

UIO-67 topology
Zr-MOFs UiO-66 series

Isoreticular Zr-MOFs

Zr-BDC-MOF

Zr-PDF-MOF

PIZOF-1 non interpenetrated

MOF-525

O. Yaghi


PIZOF's P. Berens group
High Adsorption capacity = large surface

Surface area Zeolites 200 to 900 m$^2$/g.
Surface area MOFs 200 to 6000 m$^2$/g.

Surface area NaY 900 m$^2$/g.
Surface area UiO-66 1100 m$^2$/g.
Surface area UiO-67 3000 m$^2$/g.

From: An evaluation of UiO-66 for gas-based applications
Wiersum, A. D.; Soubeyrand-Lenoir, E.; Yang, Q.; et al. CHEMISTRY-AN ASIAN JOURNAL 6, 2011, 12,3270
How does an enzyme recognize CO₂?

Julien J.H. Cotelesage\textsuperscript{a,1}, Jennifer Puttick\textsuperscript{a,1}, Hughes Goldie\textsuperscript{b}, Babak Rajabi\textsuperscript{b}, Brian Novakovski\textsuperscript{b}, Louis T.J. Delbaere\textsuperscript{a,*}

\textsuperscript{a} Department of Biochemistry, University of Saskatchewan, 107 Wiggins Road, Saskatoon, Sask., Canada S7N 5E5  
\textsuperscript{b} Department of Microbiology and Immunology, University of Saskatchewan,  
107 Wiggins Road, Saskatoon, Sask., Canada S7N 5E5

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Abstract

Phosphoenolpyruvate carboxykinase (PCK) reversibly catalyzes the carboxylation of phosphoenolpyruvate to oxaloacetate. Carbon dioxide, and not bicarbonate ion, is the substrate utilized. Assays of the carboxylation reaction show that initial velocities are 7.6-fold higher when CO₂ is used instead of HCO₃⁻. Two \textit{Escherichia coli} PCK-CO₂ crystal structures are presented here. The location of CO₂ is the same for both structures; however the orientation of CO₂ is significantly different, likely from the presence of a manganese ion in one of the structures. PCK and the other three known protein–CO₂ crystal structure complexes have been compared; all have CO₂ hydrogen bonding with a basic amino acid side chain (Arg65 or Lys213 in PCK), likely to polarize CO₂ to make the central carbon atom more electrophilic and thus more reactive. Kinetic studies found that the PCK mutant Arg65Gln increased the $K_M$ for substrates PEP and oxaloacetate but not for CO₂. The unchanged $K_M$ for CO₂ can be explained since the Arg65Gln mutant likely maintains a hydrogen bond to one of the oxygen atoms of carbon dioxide.
How does nature capture CO$_2$ from air?

RuBisCO is the most abundant protein on earth and is a crucial enzyme in carbon fixation.

It has been studied extensively by biochemical and structural methods; however, the most essential activation step has not yet been described.

The first paper describing mechanistic details on RuBisCO activation by atmospheric CO$_2$ was published only 4 months ago.

Structural mechanism of RuBisCO activation by carbamylatation of the active-site lysine. B. Stec, PNAS, 109, nov 2012, 46, 18785
Sorption enthalpy and Selectivity

How does nature capture CO$_2$ from air?

The active site is a Mg$^{2+}$ ion surrounded by carboxyl and amino ligands. The resolution is however, moderate 2.2Å.
Effect of confinement.

**Enzym RuBisCo**

Structural mechanism of RuBisCO activation by carbamylation of the active site lysine.
B. Stec, PNAS, 109, nov 2012, 46, 18785
How does nature capture CO$_2$?

Very recently (13 Feb. 2013) was a high resolution (0.9Å) structure of Human Anhydrase with CO$_2$ adsorbed deposited.

The active site is a Zn$^{2+}$ ion, but the occupancy of CO$_2$ at this site is only 0.3. But nearby is an other CO$_2$ adsorbed to an aromatic 6-ring the occupancy at this site is 0.8.
The regular UiO-66 has a surprisingly good adsorption enthalpy (26 kJ/mole).

UiO-66 with CO$_2$ adsorbed in the same position as in the enzyme Anhydrase.
Sorption enthalpy and Selectivity

Adjusting the adsorption enthalpy by adding functional groups.

Serre et al. Chem. Com., 2011, 47, 9603–9605
Sorption enthalpy and Selectivity

Adjusting the adsorption enthalpy by adding functional groups.

Serre et al. Chem. Com., 2011, 47, 9603–9605
Sorption enthalpy and Selectivity

**Current activity:** Adjusting the adsorption enthalpy by adding multiple functional groups.

UiO-67 mixed ligands 50% Bipyridine
Summary and outlook

• Knowledge about how nature capture and activate CO\(_2\) are appearing just now.

• This new knowledge coincides with our ability to go from an idea to a synthesize real nano-structured material.
  
  • But it did require 11 years of effort. (4 phd’s and 4 Post doc’s) to acquire this skill.

• We are at a turning point. The materials synthesis is to a large (some) extent under control.

• Focus can therefore now be shifted towards “design” of new materials with complex active sites.

Zr-MOF-545
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